

SOLUTION: This photocurable resin composition comprises (A) a compound having an oxetane ring, e.g. a compound of formula I [Z is O or S; R<SP>1</SP> is H, F, a 1-6C (perfluoro)alkyl, a 6-8C aryl, etc.; R<SP>2</SP> is

shaping in a short time, having small curing shrinkage and capable of developing high toughness and dimensional accuracy by curing, by including a compound having oxetane ring, an epoxy-containing compound and a cationic photopolymerization initiator.

ABSTRACT:

INT-CL (IPC): C08G059/68, B29C067/00, C08G065/18, G03F007/038

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ASSIGNEE-INFORMATION:
NAME
JSR CORP
NIPPON TOKUSHU COATING KK
COUNTRY
N/A
N/A

INVENTOR-INFORMATION:
NAME
YAMAMURA, TETSUYA
WATANABE, TAKESHI
TAKUCHI, AKIRA
UKAJI, TAKASHI

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H, a 1-6C
 alkyl, a 2-6C alkenyl, a 6-8C aryl, etc.; R<SP>2</SP> is H, a 1-6C
 alkyl, a
 2-6C alkenyl, a 6-8C aryl, etc.] or a compound of formula II
 [R<SP>3</SP> is a
 1-20C (branched)alkylene, a 1-20C (branched) poly(alkyleneoxy),
 etc.], (B) an
 molecular
 epoxy-containing compound (e.g. having 1,000 to 20,000 number-average
 weight in gel permeation chromatography) and (C) a cationic
 photopolymerization
 initiator, e.g. in a weight ratio of 30-97wt.%, 3-50wt.% and 0.1-
 10wt.%,
 respectively.

特開平10-168165

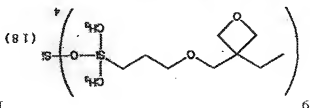
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C 0 8 G 59/68		C 0 8 G 59/68
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C 0 8 G 65/18		C 0 8 G 65/18
G 0 3 F 7/038		G 0 3 F 7/038
5 0 3		5 0 3
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(21) 出願番号	特開平8-352868	(71) 出願人 00004178
(22) 出願日	平成8年(1996)12月13日	(71) 出願人 592109732 ジェイエスエフール株式会社 東京都中央区築地2丁目11番24号
(72) 発明者		(72) 発明者 山村 哲也 東京都中央区築地2丁目11番24号
(72) 発明者		(72) 発明者 山村 哲也 東京都中央区築地2丁目11番24号
(72) 発明者		(72) 発明者 藤田 豊 東京都中央区築地2丁目11番24号
(74) 代理人		(74) 代理人 成コム株式会社内 東京都中央区築地2丁目11番24号
(74) 代理人		(74) 代理人 外間土 昌男 周志 最終頁に続く

(54) 【発明の名称】 光学的立体造形用光硬化性樹脂組成物

(57) 【要約】
 【課題】光照射によって速やかに硬化し、そのため造形が短時間で終了し、得られる硬化物が高い靱性を有し、かつ、硬化位置が小さい高いため寸法精度の高い立体形状物を得ることができる。光学的立体造形に適した光硬化性樹脂組成物を提供すること。
 【解決手段】(A) オキセタン環を有する化合物、(B) エポキシ基含有化合物、および(C) カチオン性光重合開始剤を含有する光学的立体造形用光硬化性樹脂組成物。

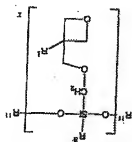


次の一般式(19)で表される化合物は1~10個のオ

キモクシ生草類の分布。

【0031】

【619】



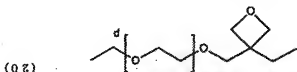
(61)

の炭素原子数に4のアルキル基または1にアルキル基(ここで、アルキル基は同一または異なる、例えはトリメチルシリル基、トリエチルシリル基、トリブチルシリル基、トリオクチルシリル基等の炭素原子数3~12のもの)であり、 n は1~10の整数を示す。

としては、上述の例以外にも、グルバール・エーシメンロアトラングで測定したポリスチレン試算の幾平均分子量1000~5000程度の高分子量を有する化合物も挙げられる。このような例として、以下の式(20)、(21)、(22)で表される化合物が挙げられ

【0033】
【420】

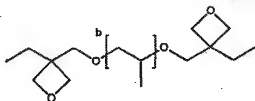
3. R11は×手1基、エチル基、アロイル基、アチル基*



※【花21】

(227, p. 200-201 of the book.)

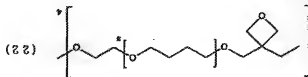
100341



* [1E2Z]

(1992年1001~511b 2.22)

100351



(ここで、 δ は20~200の整数である。)

以上説明したオキセタン環を有する化合物(A)の具体例

は次の通りである。

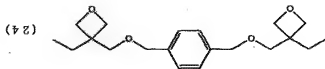
(オキセキノ環を1個有する化合物) 3-エチル-3-

ERK1/2の活性化は、3-（メチル）チロシン

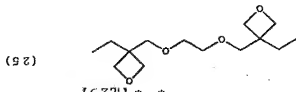
シメツルニシテ、(3-1)ノシメツルニシテ、

オキセタニル×トキシ×チル×ンゼン、A-フルオロ

[illegible][illegible]



(8)



* 【化25】



【化26】

【0038】

これらのオキセタン環を有する化合物は、1種単独であ

るいは2種以上を組み合わせ使用することができる。

【0039】本発明の樹脂組成物における(A)成分の

含有割合は、通常30～97重量%とされ、好ましくは

40～96重量%、特に好ましくは50～95重量%と

される。(A)成分の含有割合が最小である場合には、

得られる樹脂組成物のカチオン重合反応速度(硬化速

度)が小さくなり、成形に長時間を要したり、解凍度が低

下したりする傾向がある。(A)成分の含有割合が最大

である場合は、硬化物の脆性が低下したり、カチオン重

合反応速度(硬化速度)が低下する傾向にある。

(B)エポキシ基含有化合物

本発明の樹脂組成物を構成するエポキシ基含有化合物

(B)以下「(B)成分」ともいう)は、エポキシ基

を有し、グルビエーショナルプロパグレートで調

定したポリスチレン換算の数平均分子量が、得られる樹

脂組成物の粘度、成形に要する時間および得られる硬化

であることが好ましく、より好ましくは1500以上1

万以上であり、さらに好ましくは2000以上5000

40

以下である。

【0040】エポキシ基含有化合物(B)としては、例え

ば、(1)エチレン性不飽和結合を有する対応化合物の

炭素-炭素二重結合を過酸化物、過酸等の適当な酸化

剤でエポキシ化する方法により得られるエポキシ変性化

合物；(2)分子内にエポキシ基を含有するジカル重合

性モノマーを重合して得られるエポキシ基含有重合体；

(3)水酸基等の官能基を有する化合物をエチクロロエ

リ得られるエポキシ基含有化合物等が挙げられる。

※50

※【0041】エポキシ基含有化合物(B)として好ましい

とされる、前述したポリスチレン換算の数平均分子量が

1000以上2万以上であるものを得るには、上記の製

法(1)の製法の場合には、原料であるエチレン性不飽和

結合基を有する化合物としてポリスチレン換算の数平均

分子量が1000以上2万未満のものを使用すればよ

く、製法(2)の場合には、前述の重合度のポリマーが得

られるように公知の方法で調整すればよい。また、製法

(3)の場合には、原料である水酸基等の官能基を有する

化合物としてポリスチレン換算の数平均分子量が100

0以上2万未満のものを使用すればよい。

【0042】上記(1)のエポキシ変性化合物としては、

共役ジエン系モノマーの重合体、共役ジエン系モノマ

ーとエチレン性不飽和結合を有する化合物との共重合

体、ジエン系モノマーとエチレン性不飽和結合性基を有

する化合物との共重合体、天然ゴム等の(共)重合体を

エポキシ化した化合物が挙げられる。例えばジエン

系モノマー、イソプレンモノマー等の共役ジエン系モノ

マーの重合体をエポキシ化した化合物；共役ジエン系モノ

マーとエチレン、プロピレン、ブタジエン、イソプレン、

アクリレン等のエチレン性不飽和結合を有する化合物と

の共重合体をエポキシ化した化合物；エチレン性不飽和

結合基を有する化合物と、例えばジシクロヘキソジエン

等のジエン系モノマーとの共重合体をエポキシ化した化

合物；天然ゴム等の分子内に有する二重結合をエポキシ

化した化合物等が挙げられる。市販品としては、例え

ばエポキシ化ポリブタジエンとしては、P013、P014、R

45BPI(以上、出光石油化学(株))、R-1

5BPI、R-45BPI(以上、サカギ化成工業

(株))、エポリールPFB3600、PFB4700(以

* [10045] 以上例示したエポキシ基含有化合物の中で

も、(B)成分として特に好ましい具体例としては、P₀

5BP1、エポキシP₀B3を要したり、P₀B4700が導

けられる。上記のエポキシ基含有化合物は、1重量部

あるいは2種以上を組み合わせて (B) 成分を構成する

ことができる。

[10046] 本発明の樹脂組成物における (B) 成分の

含有割合は、通常3〜50重量%とされ、好ましくは4

〜40重量%とされ、さらに好ましくは5〜30重量%

とされる。(B) 成分の含有割合が減少する場合には、

得られる樹脂組成物のカチオン重合反応速度(硬化

速度)が小さくなり成形に長時間を要したり、解離度が

低下したり、硬化物の特性が低下する傾向がある。

(C) カチオン性光重合開始剤

本発明の樹脂組成物を構成するカチオン性光重合開始剤

(C) 成分、たとえば、(A)、(B) 成分のいずれか一

種を受けこる。前記 (A)、(B) 成分のいずれか一

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種を受けこる。前記 (A)、(B) 成分のいずれか一

種を受けこる。前記 (A)、(B) 成分のいずれか一

上、ジテル化学工業 (株) 等の商品名のもが挙げ

られる。アジエン-アクリン共重合体のエポキシ変性

化合物としては、エポキシレフ EBSB AT01

4、AT015、AT000 (以上、ジテル化学工業

(株) 等の商品名で入手することができるものも挙げ

られる。

[10043] 上記 (D) のエポキシ基含有重合体として

は、例えばジシラン (シラ) アクリレート、ジメチル

クロホキシエポキシエポキシ (シラ) アクリレート

シクロホキシエポキシ (シラ) アクリレート等の単純

重合体あるいは他のエポキシモノマーとの混合化合物が幸

重化合物である。これらのエポキシ樹脂の分子重量が1

000以上2万以下の範囲にあるものである。

[10044] 上記 (D) の光重合可能な重合体含有化合物

物とエポキシ樹脂との反応により得られるエポキシ

基含有化合物としては、例えば両末端水酸基含有ポリ

アクリレートとエポキシ樹脂との反応により得られ

る化合物が挙げられる。市販品としては、例えば、P

01 y b d R-45 EPT (以上、出光石油化学

(株))、R-15 EPT、R-45 EPT (以上、ナ

ガセ化成工業 (株)) 等の商品名で入手することができ

る。これらのポリアクリル樹脂の分子重量の平均

分子重量が1000以上2万以下の範囲にあるものである。

[式(27)においてエポキシ樹脂の具体例として

は、ジメチルエポキシエポキシ、4-メチルエポキシ

エポキシ、エポキシエポキシ、4-メチルエポキシ

エポキシ、エポキシエポキシ、4-メチルエポキシ

エポキシ、エポキシエポキシ、4-メチルエポキシ

エポキシ、エポキシエポキシ、4-メチルエポキシ

エポキシ、エポキシエポキシ、4-メチルエポキシ

[illegible]

一トなどを例示することができ、これらは1種単独であるいは2種以上を組み合わせて用いることができる。

1. 1972年12月1日、東京府知事の命令により、東京府立第一高等学校を東京府立第一高等学校第一学舎と改称した。

[illegible]

02 01 02 03 04 05 06 07 08 09 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006 1007 1008 1009 1010 1011 1012 1013 1014 1015 1016 1017 1018 1019 1020 1021 1022 1023 1024 1025 1026 1027 1028 1029 1030 1031 1032 1033 1034 1035 1036 1037 1038

[0063] 1分子中に2個以上のエチレン性不飽和結合を有する多官能モノマーとしては、例えばエチレニルシ(メタ)アリレート・トリレンジオキシベンジアル・アリレート・トリエチレンジオキシベンジアル・アリレート・トリジアゾロキスエチン・アリレート・トリアザロキスエチン・アリレート・ビスアリレート・トリアズマレート・トリアズ

29

【0062】これらの東宮能生ノマの市販品として
は、例えにゴキウマ-M-101、M-102、M-
1113、M-117、M-152、TO-
1210 (以上、東宮合成 (株))、カヤマツケ-
1105、R-128H (以上、日本化学
(株))、エスコ-192、エスコ-220、エス
コ-2311HP、エスコ-2000、エスコ-
21210、エスコ-2150、エスコ-87、エス
コ-17P (以上、大東有機化学工業 (株))などの
商品名で入手可能なものと考えることがきる。

示されたトリ (×) フクリール化合物、チラ (×) フクリール化合物、 α -ナ (×) フクリール化合物

【10066】かみか多官能モノとして、上記に例を挙げる。ことができる。

和崎芳子(株)、NKエナルA-BPE-4(以
上、新中村化学工業(株)などの商品名で入手のもの)

R-77, SP-4010, SP-4060 (以上、昭

ASF-400 (以上、新日鐵化学(株))、リホキシ
SP-1506 SP-1507 SP-1509 V

40 22-707777BPE-4、TEICA、BR-4
2M、GX-8345 (以上、第一工業製薬(株))、

P-4EA、BP-4PA、BP-2EA、BP-2P
A、DCP-A (以上、共栄油脂化学工業(株))、

5、M-325、M-400、M-6200、M-6400 (以上、東亞合成(株))、ライオンシリートB

5-M-305-M-309-M-310-M-311

205 (以上、日本化薬(株))、プロニックスM-2
10 M-220 M-233 M-240 M-21

040, TPA-320, TPA-330, RP-10
40, RP-2040, R-011, R-300, R-

30 DPCA-60, DPCA-120, DN-0075,
DN-2475, T-1420, T-2020, T-2

HA-2H, DPHA-2C, DPHA-2I, D-3
10, D-330, DPCA-20, DPCA-30,

2. H-604, H-684, PET-50, GPO-303, TMPA, THE-330, DPHA, DP

DA, TPQDA, MANDA, R-551, R-71

3000、E2コート3700 (以上、大阪有機化学工業(株))、カクマR-526、HDDA、NPG

20 73-1360, 73-1GPT, 73-140
0, 73-1700, 73-1540, 73-1

0. EY3-1215, EY3-1310, EY3-1
214HP, EY3-1295, EY3-1300, E

U. S. AIR FORCE (AF), AFMATSAL002 (LIE, 三機中(機)), E
X2-1195, EX2-1230, EX2-126

【10065】これらの多官能性モノマーの市販品として

ルヲロバテト云々(カ)ノリナシ

9) アクリレート、カプロラクトノ変性ジペンタエリス
リトールペンタ(84) アクリレート、ジトリルキアロ-

10 アロウクトン愛知県八ツ田町八ツ田(×)

$\sqrt{2} \approx 1.414$ (1.41421356237) $\sqrt{3} \approx 1.732$ (1.73205080757) $\sqrt{4} = 2$ (2.00000000000) $\sqrt{5} \approx 2.236$ (2.23606797750) $\sqrt{6} \approx 2.449$ (2.44948974278) $\sqrt{7} \approx 2.646$ (2.64575131106) $\sqrt{8} \approx 2.828$ (2.82842712475) $\sqrt{9} = 3$ (3.00000000000) $\sqrt{10} \approx 3.162$ (3.16227766017) $\sqrt{11} \approx 3.317$ (3.31662479036) $\sqrt{12} \approx 3.464$ (3.46410161514) $\sqrt{13} \approx 3.606$ (3.60555127546) $\sqrt{14} \approx 3.742$ (3.74165738677) $\sqrt{15} \approx 3.873$ (3.87298334621) $\sqrt{16} = 4$ (4.00000000000) $\sqrt{17} \approx 4.123$ (4.12310562562) $\sqrt{18} \approx 4.243$ (4.24264068712) $\sqrt{19} \approx 4.359$ (4.35889894354) $\sqrt{20} \approx 4.472$ (4.472135955)

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変性トリメチロル(×6)トリ(×6)アクリル

ロ-ルアロ/ベトリ (X4) アクリレート、EO 変性ト
リメチル-ルアロ/ベトリ (X4) アクリレート、EO

*ノール3gを仕込んだ。次に、ヒドロキシエチルアリ

レート1730gを、温度を20℃以下に制御しながら

添加した。添加後、さらに10-20℃で1時間加熱を

継続した後、3-メチル-1,5-ヘンタノジオールと

アジピン酸からなる数平均分子量1000のポリエス

テル「P-1010」(株)クラレ製)745

gを、温度40-50℃に保ちながら添加した。次に、反応を終

了させ、数平均分子量が約1680のγブチラクトンアリ

レート「U-1」を得た。

【0082】該反応脂組成物の調整

調整機を備えた反応容器に、γブチラクトンアリレート「U

-1」を36重量部、反応希釈剤としてトリシロプロパ

ノールジメチルシリレート18重量部、イソ

ノルブチルアリレート23重量部、アロキシルモノル

クトン7重量部、光阻剤として1-ヒドロキシエニル

脂組成物を得た。

【0083】

【表1】

※50

性が良いということは、照射光量が変化しても、得られ

る、曲げ弾性率などに影響を与える。すなわち、光硬化

度)であり、硬化度は硬化物の力学特性、例えばヤング

模量)を調節する。硬化度は硬化物において架橋反応の程度(硬化

度)である。硬化度は硬化物の力学特性、例えばヤング

模量)を調節する。硬化度は硬化物において架橋反応の程度(硬化

度)である。硬化度は硬化物の力学特性、例えばヤング

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〔立体形状物の造形性〕立体形状物の造形性の評価は、写真照像から造形された立体形状物の寸法精度と造形に

設置(商品名)ソリックスターSCS-1000H

水平なはりかとも断面が一辺6.4mmの正方形であり、柱の長さが44.5mmではりの長さ

【0087】 透視された立体形状物は、温度23℃、相対湿度50%の恒温恒湿室内に24時間静置することに

(i) 液面におけるレーザー光強度: 1.0 mW
(ii) 走行速度: 各種脂類成分において硬化率が0.

(2) 立体形状物の寸法精度の測定：得られたH型立体

(1)、(II)により求めた寸法AとBの差、寸法CとBの差から立体形状物の寸法精度を評価した。

(II) $C-B$ の寸法差 = (C-B) (3) 造形時間の測定

【0089】
【卷2】

(1) 試験片の作製：アクリクータを用い、ガラス板上より行った。

311-00型)を用いて、当該布膜の表面に紫外線

相対湿度50%の恒温恒湿室内に1時間静置することにより試験片を調整し、測定に供した。

引張速度 1 mm/min 、標線間距離 25 mm の条件でヤング率を測定した。測定は引張り試験機（島津製作所

【0085】〔硬化フイルムの特性〕硬化物の特性は、外部から与えられる応力による増れにくさを表すもので

(1) 試験片の作成

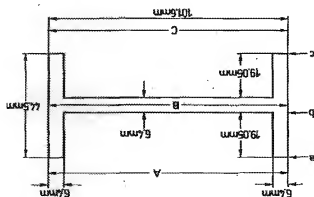
て、当該被布膜の表面に紫外線を照射（照射量5.0 mJ/cm²）して、完全に硬化しないうちに照射を中止

に載せ、最初に紫外線を照射した面とは反対側の面から紫外線を照射（照射量 50 mJ/cm^2 ）して、硬

℃、相対湿度50%の恒温恒湿室内に24時間静置することにより試験片を作成し、測定に供した。

フロッピーディスクの読み

(72) 発明者 竹内 章
 東京都中央区築地二丁目11番24号 日本合
 成工業株式会社内
 (72) 発明者 宇加地 孝志
 東京都中央区築地二丁目11番24号 日本合
 成工業株式会社内



【図1】

* NOTICES *

JP0 and INPT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the photo-setting resin constituent for optical solid modeling.

[0002]

[Description of the Prior Art] By repeating the process of carrying out an optical exposure selectively and forming a cured resin layer in the liquefied substance of a photorealist in recent years, the optical solid modeling method the cured resin layer concerned forms the cubic shape thing which it comes to laminate in one is proposed (JP,60-247515,A). Refer to U.S. Pat. No. 4,575,330 (JP,62-35966,A), JP,62-101408,A, and JP,5-24119,A.

[0003] Explanation of the typical example of this optical solid modeling method will form the cured resin layer which has a predetermined pattern by irradiating selectively the oil level of the liquefied substance (photo-setting resin constituent) of a photorealist accommodated in the container with lights, such as ultraviolet laser. Subsequently, laminating formation of the new cured resin layer is carried out in one so that this may be followed on the cured resin layer of a part further, and irradiating that oil level selectively. And the cubic shape thing in which it comes to laminate two or more cured resin layers in one is formed by the number of predetermined times repeating the above-mentioned process, without making it change, changing the pattern in which light is irradiated. Even if this optical solid modeling method has the complicated shape of the cubic shape thing made into the purpose, since it can moreover obtain easily in a short time, it attracts attention.

[0004] As a photo-setting resin constituent used for the optical solid modeling method in the former, it is the following. (b)-[**] A resin composition [like] is publicly known.

(b) Urethane (meta) acrylate, oligoesters (meta) acrylate, The resin composition containing

radical polymerization nature organic compounds, such as epoxy (meta) acrylate, a thiol and an ene compound, and photosensitive polyimide (for example, refer to JP,1-204915,A, JP,2-208305,A, and JP,3-160013,A).

[**]The resin composition containing cationic polymerization nature organic compounds, such as an epoxy compound, cyclic ether compound, annular lactone compound, cyclic acetal compound, annular thioether compound, and spiro orthoester compound and a vinyl ether compound (for example, refer to JP,1-213304,A).

[**]The resin composition containing a radical polymerization nature organic compound and a cationic polymerization nature organic compound (for example, refer to JP,2-28261,A, JP,2-75618,A, and JP,6-228413,A).

[0005]

[Problem(s) to be Solved by the Invention]However, the photo-setting resin constituent used for such a solid modeling method is required to harden promptly by optical exposure while viscosity can form a smooth oil level low promptly from a viewpoint of performing the efficient Mitsuzo form. It not being what swells the hardened material for which a cubic shape thing is constituted, and the thing with small deformation, such as lifting of a projecting part, resulting from the cure shrinkage at the time of photo-curing which curves and is over are required of the photo-setting resin constituent concerned.

[0006]Although the cubic shape thing obtained by the optical solid modeling method is used as a master of the prototype for the model for considering a design, and function confirmation, and a mold, etc., The cubic shape thing to use especially as a prototype of function confirmation is required to have sufficient mechanical strength which can bear that processing faithful to engineering drawing is performed in high accuracy, and a service condition, toughness, heat resistance, and moisture resistance etc.

[0007]However, conventionally, the above-mentioned demand is not satisfied enough and a publicly known resin composition describes it above, for example, (b) Urethane (meta) acrylate, oligoesters (meta) acrylate, The problem that the cubic shape thing concerned changes temporally for the residual strain resulting from cure shrinkage (lifting of a projecting part) is one of those [cubic shape] which are produced by the Mitsuzo form carrying out the resin composition containing optical radical polymerization nature organic compounds, such as epoxy (meta) acrylate. [curve and] Although the problem by such temporal modification is solvable to some extent by amendment of input CAD data, etc., it cannot fully cope with it depending on amendment of input CAD data with complication of the shape in these days, minuteness making, and diversification of an operating environment.

[0008]When performing the Mitsuzo form using the resin composition containing the optical cationic polymerization nature organic compound containing the epoxy compound of (**), it has the fault that the photo-curing speed of resin liquid is slow as compared with an optical radical

polymerization nature resin composition, and the time which modeling takes is long. The cubic shape thing obtained using the optical cationic polymerization nature resin composition which contains a publicly known epoxy compound conventionally is not fully provided with the toughness required of the prototype of function confirmation, etc.

[0009]moreover, Photo-curing speed sufficient with the hybrid type photo-setting resin constituent of the acrylate monomer and the epoxy compound which is cationic polymerization nature compounds, for example (meta) which are optical radical polymerization nature compounds cannot be obtained.

[0010]This invention is made in order to solve the problem of the above conventional technologies.

[0011]The purpose of this invention is to provide the resin composition for optical solid modeling which is completed for a short time in order to harden promptly by optical exposure, and has toughness with an expensive hardened material obtained in the top where cure shrinkage is small, and has close dimensional accuracy.

[0012]

[Means for Solving the Problem]A photo-setting resin constituent for optical solid modeling of this invention contains a compound which has the (A) oxetane ring, the (B) epoxy group containing compound, and (C) cationic photopolymerization initiator.

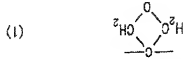
[0013]

[Embodiment of the invention]

(A) It is following formulas the compound (A) which has an oxetane ring which constitutes the photo-setting resin constituent for optical solid modeling of compound this invention which has an oxetane ring (henceforth a "resin composition"), and (it also called the following "(A)

ingredient" (1), : [0014]

[Formula 1]



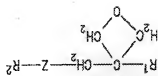
It is a compound which comes out and has one or more oxetane rings expressed. This compound causes a polymerization reaction and crosslinking reaction by carrying out an optical exposure under existence of a cationic polymerization nature photopolymerization initiator.

[0015]As a compound (A) which has such an oxetane ring, if it is a compound which has one or more oxetane rings, various things can be used. It illustrates below.

[0016]As a compound which has one oxetane ring, the compound etc. which are shown with a following general formula (2) are mentioned.

[0017]

[Formula 2]



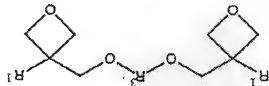
(2)

General formula (2) Setting, Z shows an oxygen atom or a sulfur atom. R¹ A hydrogen atom, a fluorine atom, a methyl group, an ethyl group, a propyl group, a furyl group, or a thienyl group with 6-18 carbon atoms, such as number of carbon atoms 1-6 piece alkyl groups, such as a butyl group, a trifluoromethyl group, a perfluoro ethyl group, and a perfluoro propyl group, a phenyl group,

and a naphthyl group. R² Number of carbon atoms 1-6 piece alkyl groups, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, and a butyl group, 1-propenyl group, 2-propenyl group, a 2-methyl-1-propenyl group, A 2-methyl-2-propenyl group, 1-butenyl group, 2-butenyl group, Number of carbon atoms 2-6 piece alkenyl groups, such as 3-butenyl group; A phenyl group, An aryl group with 6-18 carbon atoms, such as a naphthyl group, an ANTONIRU group, and a phenan tolyl group; Benzyl, Fluorobenzyl, a methoxybenzyl group, a phenethyl group, a styryl group, An aralkyl group with the substitution of a cinnamyl group, an ethoxybenzyl group, etc., or 7-18 unsubstituted carbon atoms; A phenoxyethyl group, The basis which has an aromatic ring of others, such as aryloxy alkyls, such as a phenoxyethyl group; An ethyl carbonyl group, Number of carbon atoms 2-6 piece alkyl carbonyl groups, such as a propylcarbonyl group, an ethyl carbonyl group, An ethoxycarbonyl group, Number of carbon atoms 2-6 piece alkoxy carbonyl groups, such as a carbodopropoxy group and a butoxycarbonyl group; An ethylcarbonyl group, a propylcarbonyl group, a butylcarbonyl group, They are number of carbon atoms 2-6 piece N-alkyl carbamoyl groups, such as a pentylcarbamoyl group, etc.

[0018] As a compound which has two oxetane rings, a compound etc. which are shown with a following general formula (3) are mentioned.

[Formula 3]

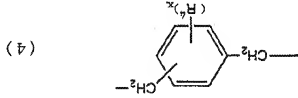


(3)

[0019] In a general formula (3), R¹ is as the definition in said general formula (2), R³, for example lines, such as ethylene, a propylene group, and a butylene group, or the letter of

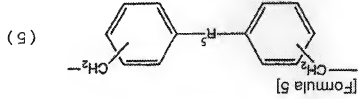
branching. Usually, an alkylene group with 1-20 carbon atoms, a poly(ethyleneoxy) group, Lines, such as a poly (propyleneoxy) group, or the letter of branching usually A poly (alkyleneoxy) group with 1-20 carbon atoms. They are an alkylene group containing the unsaturated hydrocarbon group of lines, such as a propenylene group, a methylpropenylene group, and a butenylene group, or the letter of branching, a carbonyl group, and a carbonyl group, an alkylene group which contains a carbonyl group in the middle of a chain, an alkylene group which contains a carbamoyl group in the middle of a chain, etc. The basis of the ** value chosen from the basis shown with the following general formula (4), (5), and (6) may be sufficient as R³.

[0020]
[Formula 4]



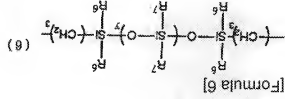
R⁴ in a general formula (4) A hydrogen atom, a methyl group, an ethyl group, Number of carbon atoms 1-4 piece alkyl groups, such as a propyl group and a butyl group, a methoxy group, It is halogen atoms, such as number of carbon atoms 1-4 piece alkoxy groups, such as an ethoxy basis, a propoxy group, and a butoxy group, a chlorine atom, and a bromine atom, a nitro group, a cyano group, a silyl group, a low-grade alkyl carboxyl group, a carboxyl group, or a carbamoyl group, and x is an integer of 1-4.

[0021]

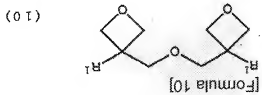
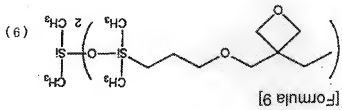
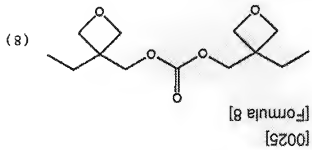
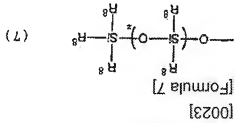


In a general formula (5), R⁵ is an oxygen atom, a sulfur atom, a methylene group, -NH-, -SO-, -SO₂-, -C(CF₃)₂-, or -C(CH₃)₂-.

[0022]

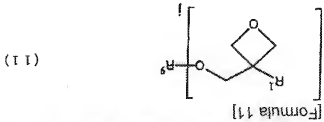


In a general formula (6), R^6 is an aryl group with 6-18 carbon atoms, such as number of carbon atoms 1-4 piece alkyl groups, such as a methyl group, an ethyl group, a propyl group, and a butyl group, a phenyl group, and a naphthyl group. y is an integer of 0-200. R^7 is an aryl group with 6-18 carbon atoms, such as number of carbon atoms 1-4 piece alkyl groups, such as a methyl group, an ethyl group, a propyl group, and a butyl group, a phenyl group, and a naphthyl group, and a naphthyl group, which are shown as mentioned with the following formula (7), (9), and (10).

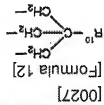


In a formula (10), R^1 is as the definition in said general formula (2).

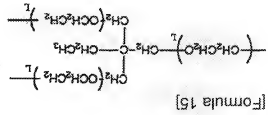
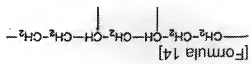
[0026] As a compound which has three or more oxetane rings, a compound etc. which are shown with a following general formula (11) are mentioned.



in a general formula (11), R^1 is as the definition in said general formula (2). The letter of branching or a linear alkylene group with 1-30 carbon atoms which R^9 shows the organic group of 3 - 10 value, for example, are shown by following formula (12) - (14), such as a basis. A line or a letter polysiloxane content group of branching shown by the letter poly (alkyleneoxy) group of branching, a following formula (16), or formulas (17), such as a basis shown with a following formula (15), is mentioned. j shows the integer of 3-10 equal to the valence of R^9 .



in a formula (12), R^{10} is number of carbon atoms 1-6 piece alkyl groups, such as a methyl group, an ethyl group, and a propyl group.]



[0029]

$$(16) \quad \begin{array}{c} \text{CH}_3 \\ | \\ \text{—CH}_2\text{—CH—CH}_2\text{—CH—CH}_2\text{—} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{—O—} \begin{array}{c} \text{CH}_3 \\ | \\ \text{—CH}_2\text{—CH—CH}_2\text{—CH—CH}_2\text{—} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$$
$$\begin{array}{c}
 \text{---} \text{S}(\text{CH}_3) \text{---} \\
 | \\
 \text{O} \\
 | \\
 \text{---} \text{S}(\text{CH}_3) \text{---} \text{O} \text{---} \text{S}(\text{CH}_3) \text{---} \text{O} \text{---} \text{S}(\text{CH}_3) \text{---} \\
 | \quad | \quad | \quad | \\
 \text{CH}_3 \text{O} \quad \text{CH}_3 \text{O} \quad \text{CH}_3 \text{O} \quad \text{CH}_3 \text{O} \\
 | \quad | \quad | \quad | \\
 \text{---} \text{S}(\text{CH}_3) \text{---} \text{O} \text{---} \text{S}(\text{CH}_3) \text{---} \text{O} \text{---} \text{S}(\text{CH}_3) \text{---} \\
 | \\
 \text{O} \\
 | \\
 \text{---} \text{S}(\text{CH}_3) \text{---}
 \end{array}$$

[0030]

(18)

ក្រុមហ៊ុន.

[0031]

(6 1)

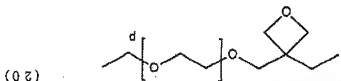
http://www4.ipdl.inp.it.go.jp/cgi-bin/tran_web.cgi_ejje?atw_n=http%3A%2F%2Fwww4.jp... 3/11/2008

carbon atoms, such as a methyl group, an ethyl group, a propyl group, and a butyl group, an alkyl group is the same or different, for example, is a thing with 3-12 carbon atoms, such as a trimethylsilyl group, a triethyl silyl group, a TORIPURO pill silyl group, and a tributyl silyl group. -- it is - r shows the integer of 1-10.

[0032] The compound which has the with a number average molecular weight of about 1000 to 5000 of the polystyrene conversion measured with gel permeation chromatography besides the above-mentioned example amount of polymers as a compound (A) which has an oxetane ring is also mentioned. The compound expressed with the following formulas (20), (21), and (22) as such an example is mentioned.

[0033]

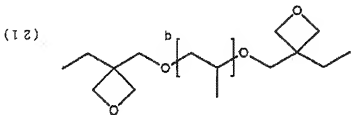
[Formula 20]



(Here, p is an integer of 20-200.)

[0034]

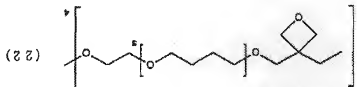
[Formula 21]



(Here, q is an integer of 15-100.)

[0035]

[Formula 22]



(Here, s is an integer of 20-200.)

The example of a compound (A) of having the oxetane ring explained above is as follows.
<Compound which has one oxetane ring> 3-ethyl-3-hydroxyethyl oxetane, 3-(meta-aryloxy)methyl 3-ethyl oxetane, methylbenzene (3-ethyl-3-OKISETA nil methoxy), 4-fluoro- [1-(3-ethyl-3-OKISETA nil methoxy) methyl] Benzene, 4-methoxy- [1-(3-ethyl-3-OKISETA nil methoxy) methyl] Benzene, [1-(3-ethyl-3-OKISETA nil methoxy) ethyl] Phenyl ether,

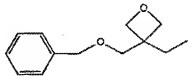
isobutoxyethyl (3-ethyl-3-OKISETA nil methyl) ether, isobomyl oxyethyl (3-ethyl-3-OKISETA nil methyl) ether, isobomyl (3-ethyl-3-OKISETA nil methyl) ether, Ethyl diethylene-glycol (3-ethyl-3-OKISETA nil methyl) ether, Dicyclopentadiene (3-ethyl-3-OKISETA nil methyl) ether, JISHIKURO pentenylkoxyethyl (3-ethyl-3-OKISETA nil methyl) ether, JISHIKURO pentenyl (3-ethyl-3-OKISETA nil methyl) ether, Tetrahydrofurfuryl (3-ethyl-3-OKISETA nil methyl) ether, Tetrabromo phenyl (3-ethyl-3-OKISETA nil methyl) ether, 2-tetrabromo phenoxyethyl (3-ethyl-3-OKISETA nil methyl) ether, 2-tribromomophenoxyethyl (3-ethyl-3-OKISETA nil methyl) ether, 2-hydroxyethyl (3-ethyl-3-OKISETA nil methyl) ether, 2-hydroxypropyl (3-ethyl-3-OKISETA nil methyl) ether, Butoxyethyl (3-ethyl-3-OKISETA nil methyl) ether, Pentachlorophenyl (3-ethyl-3-OKISETA nil methyl) ether, bornyl (3-ethyl-3-OKISETA nil methyl) ether, etc.

<Example of a compound which has two or more oxetane rings> 3,7-bis(3-OKISETANIRU)-5-oxetane, 3,3' - (1,3-(2-MECHIRENIRU) propanediyl screw (oxymethylene)) Bis-(3-ethyl-3-OKISETA nil methoxy) ethane, 1,3-bis[(3-ethyl-3-OKISETA nil methoxy) methyl] propane, Ethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, JISHIKURO pentenyl bis(3-ethyl-3-OKISETA nil methyl) ether, Theethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, Tetraethylene glycol bis(3-ethyl-3-OKISETA nil methyl) ether, Trimethylolpropanetri(3-ethyl-3-OKISETA nil methyl) ether, 1,4-bis(3-ethyl-3-OKISETA nil methoxy)butane, 1,6-bis(3-ethyl-3-OKISETA nil methoxy)hexane, Pentaerythritol tri(3-ethyl-3-OKISETA nil methyl) ether, pentaerythritol tetakis (3-ethyl-3-OKISETA nil methyl) ether, Dipentaerythritol hexakis(3-ethyl-3-OKISETA nil methyl) ether, Caprolactone denaturation dipentaerythritol hexakis(3-ethyl-3-OKISETA nil methyl) ether, Caprolactone denaturation dipentaerythritol pentakis (3-ethyl-3-OKISETA nil methyl) ether, Dimethylol propane tetakis (3-ethyl-3-OKISETA nil methyl) ether, EO denaturation bisphenol A bis(3-ethyl-3-OKISETA nil methyl) ether, PO denaturation bisphenol A bis(3-ethyl-3-OKISETA nil methyl) ether, EO denaturation hydropolymerization bisphenol A bis(3-ethyl-3-OKISETA nil methyl) ether, PO denaturation bisphenol F (3-ethyl-3-OKISETA nil methyl) ether, etc. It can illustrate, and these can be independent one sort or can be used combining two or more sorts. [0036] As a compound which has an oxetane ring which can be especially used conveniently as a (A) ingredient of a resin composition of this invention also in these, for example, methylbenzene shown by the following formula (23) (3-ethyl-3-OKISETA nil methoxy), 1,4-bis(3-ethyl-3-OKISETA nil methoxy) benzene shown by a formula (24), 1,2-bis(3-ethyl-3-

OKISETA nil methoxyethane shown by a formula (25), trimethylopropanetri(3-ethyl-3-OKISETA nil methyl) ether shown by a formula (26), and a compound expressed with said general formula (19) are mentioned.

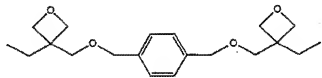
[0037]

[Formula 23]



(23)

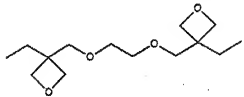
[Formula 24]



(24)

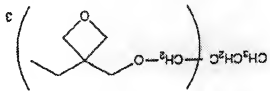
[0038]

[Formula 25]



(25)

[Formula 26]



(26)

the compound which has these oxetane rings is one-sort independent -- it is -- it can be used combining two or more sorts.

[0039] The content ratio of the (A) ingredient in the resin composition of this invention is usually made into 30 to 97 % of the weight, and is especially made into 50 to 95 % of the weight

preferably 40 to 96% of the weight. (A) When too little [the content ratio of an ingredient], the cationic polymerization reaction velocity (cure rate) of the resin composition obtained becomes small, and there is a tendency for modeling to take a long time or for resolution to fall. (A)

When the content ratio of an ingredient is excessive, be in the tendency for the toughness of a hardened material to fall or for cationic polymerization reaction velocity (cure rate) to fall. (B) The epoxy group containing compound (B) which constitutes the resin composition of epoxy

group containing compound this invention, and (it is also called the following "(B) ingredient"). The number average molecular weight of the polystyrene conversion which has an epoxy group and was measured with gel permeation chromatography in that the viscosity of the resin composition obtained, the time which modeling takes, and the toughness of hardened material acquired become better, it is preferred that it is [or more 1000] 20,000 or less, it is 10,000 or less [1500 or more] more preferably, and is 5000 or less [2000 or more] still more preferably.

[0040] As an epoxy group containing compound (B), it is (1), for example, A carbon-carbon double bond of a correspondence compound which has ethylene nature unsaturation bond groups Hydrogen peroxide, Epoxy denaturation compound; (2) obtained by a method of epoxidating with suitable oxidizers, such as a peroxy acid, a radical polymerization nature monomer which contains an epoxy group in intramolecular is polymerized. Epoxy group content polymer; (3) obtained An epoxy group containing compound etc. which are obtained by a manufacturing method with a method publicly known in itself of making a compound which has functional groups, such as a hydroxyl group, react to epichlorohydrin, etc. are mentioned. [0041] In order for a number average molecular weight of polystyrene conversion which is made desirable as an epoxy group containing compound (B) and which was mentioned above to obtain or more 1000 a thing which is 20,000 or less, in the case of a process of the above-mentioned process (1), a number average molecular weight of polystyrene conversion should just use or more 1000 less than 20,000 thing as a compound which has the ethylene nature unsaturation bond groups which is a raw material, Process (2) What is necessary is just to adjust to a case by a publicly known method so that polymer of a desired degree of polymerization may be obtained. Process (3) A number average molecular weight of polystyrene conversion should just use or more 1000 less than 20,000 thing for a case as a compound which has functional groups, such as a hydroxyl group which is a raw material. [0042] Above (1) As an epoxy denaturation compound, A compound which epoxidated polymers (**), such as a polymer of a conjugated diene system monomer, a copolymer of a conjugated diene system monomer and a compound which has ethylene nature unsaturation bond groups, a copolymer of a diene system monomer and a compound which has an ethylene nature unsaturation unit group, and crude rubber, is mentioned. For example, a compound which epoxidated a polymer of conjugated diene system monomers, such as a butadiene monomer and an isoprene monomer, A conjugated diene system monomer and ethylene, A compound which epoxidated a copolymer with a compound which has ethylene nature unsaturation bond groups, such as propylene, a butene, isobutylene, and styrene; A compound which has ethylene nature unsaturation bond groups, For example, a compound which epoxidated a copolymer with diene system monomers, such as a dicyclopentadiene, a compound etc. which epoxidated a double bond which it has in intramoleculars, such as crude

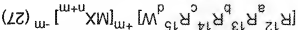
rubber, are mentioned. As a commercial item, for example as epoxidation polybutadiene, A thing of trade names, such as Poly bd R-45 EPI (above, Idemitsu Petrochemistry), R-15EPI, R-45EPI (above, Negase Brothers Chemical Industry), and EPOL-EAD PB3600 and PB4700 (above, Daicel Chemical Industries, Ltd.), is mentioned. As an epoxy denaturation compound of Butadiene Styrene, he is the EPO friend. What can be obtained with trade names, such as ESBS AT014, AT015, and AT000 (above, Daicel Chemical Industries, Ltd.), is mentioned. [0043] Above (2) As an epoxy group content polymer, for example, glycidyl (meta) acrylate, vinyl cyclohexene oxide, 4-vinylpoxycyclohexane, 3,4-epoxycyclohexylmethyl (meta) acrylate, Homopolymers, such as caprolactone denaturation 3,4-epoxycyclohexylmethyl (meta) acrylate, or a copolymer with other vinyl system monomers is mentioned, and these have a number average molecular weight of polystyrene conversion in or more 1000,20,000 or less range.

[0044] Above (3) As an epoxy group containing compound obtained by the reaction of a compound and epichlorohydrin which have functional groups, such as a hydroxyl group, a compound etc. which are obtained, for example by the reaction of both-ends hydroxyl group content polybutadiene and epichlorohydrin are mentioned. As a commercial item, it is Poly bd R-45 EPT (above), for example, What can be obtained with trade names, such as Idemitsu Petrochemistry, R-15EPT, and R-45EPT (above, Negase Brothers Chemical Industry), is mentioned, and these have a number average molecular weight of polystyrene conversion in or more 1000,20,000 or less range.

[0045] Also in an epoxy group containing compound illustrated above, Poly bd R-45EPI, R-15EPI, R-45EPI, and EPOL-EAD PB3600 and PB4700 are especially mentioned as a desirable example as a (B) ingredient, the above-mentioned epoxy group containing compound is one-sort independent -- it is -- the (B) ingredient can be constituted combining two or more sorts. [0046] A content ratio of the (B) ingredient in a resin composition of this invention is usually made into 3 to 50 % of the weight, is preferably made into 4 to 40 % of the weight, and is made into 5 to 30 % of the weight still more preferably. (B) When too little [a content ratio of an ingredient], cationic polymerization reaction velocity (cure rate) of a resin composition obtained becomes small, and there is a tendency for modeling to take a long time, for resolution to fail, or for the toughness of a hardened material to fail. (B) When a tendency ratio of an ingredient is excessive, viscosity of a resin composition increases and be in a tendency for modeling to take a long time. (C) When a cationic photopolymerization initiator (C) which constitutes a resin composition of cationic photopolymerization this invention, and (it is also called the following "(C) Ingredient") receive energy lines, such as light, they are the above (A) and a compound which makes cationic polymerization of the (B) ingredient start.

[0047] Cationic photopolymerization initiator (C) Onium salt which has the structure expressed with a following general formula (27) as a desirable example can be mentioned. This onium

salt is a compound which emits Lewis acid by receiving light.



[A cation is onium ion among a formula and W S, Se, Te, P, it is As, Sb, Bi, O, I, Br, Cl, or N*, and R¹², R¹³, R¹⁴, and R¹⁵ are the same or different organic groups, a, b, c, and d are the integers of 0-3, respectively, and their (a+b+c+d) is equal to a valence of W. M is a halogenide complex. It is metal or metalloid which constitutes a neutral atom of [MX^{n+m}], for example, they are B, P, As, Sb, Fe, Sn, Bi, aluminum, Ca, In, Ti, Zn, Sc, V, Cr, Mn, Co, etc. X is halogen atoms, such as F, Cl, and Br, m is an electric charge of net of halogenide complex ion, and n is a valence of M.]

In a general formula (27), as an example of onium ion, Diphenyliodonium, 4-methoxy diphenyliodonium, bis(4-methylphenyl)iodonium, Bis(4-tert-butylphenyl)iodonium, bis (dodecylphenyl)iodonium, Triphenylsulfonium, diphenyl-4-thiophenoxyphenyl sulfonium, A bis [4-(diphenylsulfonio)-phenyl] sulfide, a bis[4-(4-(2-hydroxyethyl) phenyl) sulfonio]-phenyl] sulfide, eta⁵-2,4-(cyclopentadienyl) [benzene [1,2,3,4,5,6-eta-(methylene)]-]-iron (1+) etc. are mentioned.

[0048]As an example of negative ion (MX^{n+m}) in the above-mentioned general formula (27),

Tetrafluoroborate (BF⁴), hexafluorophosphate (PF⁶), Hexafluoroantimonate (SbF⁶),

hexafluoroarsenate (AsF⁶), hexachloro antimonate (SbCl⁶), etc. are mentioned, cationic

photopolymerization initiator (C) ***** -- in said general formula (27) as onium salt which can

be used -- instead of [or [MX^{n+m}]] -- general formula: [MXⁿ(OH)ⁿ]

(here, M, X, and n are as a definition about a general formula (27).) -- negative ion expressed. A perchlorate ion (ClO⁴), trifluoromethylsulfonic acid ion (CF³SO³), Onium salt which has

other negative ion, such as fluoro-sulfonic acid ion (FSO³), toluenesulfonic acid ion,

trinitrobenzenesulfonic acid ion, and trinitrotoluenesulfonic acid ion, is mentioned.

[0049]Cationic photopolymerization initiator (C) It carries out and there is aromatic onium salt as an example of usable onium salt. For example, an aromatic halo NIMU salt given in

JP,50-161996,A, JP,50-158680,A, etc., JP,50-151997,A, JP,52-30899,A, VA fellows aromatic onium salt given in VIA fellows aromatic-onium-salt: JP,50-158698,A given in JP,56-55420,A,

JP,55-125105,A, etc.; JP,56-8428,A, Aromatic diazonium salt given in oxo sulfonium salt;

JP,49-17040,A given in JP,56-149402,A, JP,57-192429,A, etc.; a thio kinky thread RIIMU salt; given in a U.S. Pat. No. 4,139,655 specification etc. are preferred. Iron / allene complex, an

aluminum complex / photoysis silicon compound system initiator can be mentioned.

[0050](C) As a commercial item of a cationic photopolymerization initiator which can be used

as an ingredient, UVI-6950 and UVI-6970 (screw [— 4- (4-(2-hydroxyethyl) phenyl) sulfonio] - phenylsulfide); [for example,] UVI-6974(screw [4-diphenylsulfonio]-phenyl) A mixture of sulfide screw hexafluoroantimonate and diphenyl-4-thio phenoxyphehyl sulfonilumhexafluoroantimonate, UVI-6990 (above) (salt of hexafluorophosphate of UVI6974) Union Carbide and ADEKAOPUTOMA SP-151 and SP-170 (screw [— 4- (4-(2-hydroxyethyl) phenyl) sulfonio] - phenylsulfide); SP-150 (hexafluorophosphate of SP-170), SP-171 (above) Asahi Denka Kogyo K.K., Irgacure 261 (eta⁵-2,4-cyclopentadiene 1-yl) [(1,2,3,4,5,6-eta) - (1-methylethyl) benzene]-iron (1+)-hexafluorophosphate (1-) (above, Ciba-Geigy, CI-2481, CI-2624, CI-2639, CI-2064 (above, Nippon Soda Co., Ltd.), CD-1010, CD-1011, CD-1012 (above) (4-(2-hydroxytetradeca nil oxy) diphenyliodonilumhexafluoroantimonate) Sartomer, DTS-102, DTS-103, NAT-103, NDS-103 (- dimethyl sulfonilumhexafluoroantimonate) (4-triphenylsulfonilum hexafluoroantimonate), MDS-103 (4-methoxyphehyl diphenyl hydroxynaphthyl), TFS-102 (triphenylsulfonilumhexafluorophosphate), TFS-103 iodonilum hexafluorophosphate), BBI-103 (above, Green Chemicals) (bis(4-tert-phenyl) BBI-101 (bis(4-tert-butylphenyl)iodonilum tetrafluoroborate), BBI-102 (bis(4-tert-butylphenyl) iodonilum hexafluorophosphate), What can be obtained with trade names, such as Degacure K126 (screw [phenyl] 4-(diphenylsulfonio)-]] sulfide screw hexafluorophosphate) (made by Degussa AG), is mentioned, UVI-6970, UVI-6974, ADEKAOPUTOMA SP-170, SP-171, CD-1012, and MPI-103 can use it preferably among these. However, it is not limited to these illustration.

[0051]the above-mentioned cationic photopolymerization initiator is one-sort independent -- it is -- the (C) ingredient can be constituted combining two or more sorts of things. [0052]A content ratio of the (C) ingredient in a resin composition of this invention is usually made into 0.1 to 10 % of the weight, and is preferably made into 0.3 to 3 % of the weight still more preferably 0.2 to 5% of the weight. (C) When too little [a content ratio of an ingredient], the photoresist of a resin composition obtained cannot fall and a cubic shape thing which has sufficient mechanical strength cannot be modeled. When presenting the optical solid modeling method with a resin composition obtained on the other hand when this content ratio is excessive, a suitable light transmittance state (hardening depths) cannot be acquired, but there is a tendency for mechanical strengths, such as toughness, to fall, about a cubic shape thing obtained.

in addition, in a range which does not spoil an effect of this invention in a resin composition of ingredient this invention, it is the above-mentioned essential ingredient. [(A) ingredient - (C) ingredient] An ingredient of an except can be made to contain if needed. [0053]As such an arbitrary ingredient, cationic polymerization nature or compounds other than the (A) ingredient and the (B) ingredient can be mentioned first. A cationic polymerization

nature compound is a compound which has an organic group which causes a polymerization reaction and crosslinking reaction under existence of acid or a cation. For example, epoxy compounds other than the (B) ingredient, an oxo run compound, a cyclic acetal compound, an annular lactone compound and thirane compound, a thietane compound, a vinyl ether compound, A spiro orthoester compound, ethylene nature unsaturated compound, cyclic ether compound, annular thioether compound, and vinyl compound etc. which are resultants of an epoxy compound and lactone can be mentioned. Specifically, it is as follows.

[0054] As epoxy compounds other than an ingredient, for example (B) Alicyclic epoxy compound; 3,4'-epoxy cyclohexane carboxylate, 2-(3,4'-epoxycyclohexyl) 5,5'-spiro 3,4'-epoxy cyclohexane-metha- dioxane, A bis(3,4'-epoxycyclohexyl) horse mackerel peat, vinyl cyclohexene oxide, 4-epoxy-6-methylcyclohexane, a bis(3,4'-epoxy-6-methylcyclohexyl) horse mackerel peat, 3,4'-vinylepoxy cyclohexane, a bis(3,4'-epoxy-6-methylcyclohexyl) horse mackerel peat, 3,4'-epoxy-6-methylcyclohexyl 3,4'-epoxy-6-methylcyclohexane carboxylate, Methylenebis (3,4'-epoxy cyclohexane), dicyclopentadiene diepoxide, 11 (3,4'-epoxycyclohexyl) ether of ethylene glycol, An ethylene screw (3,4'-epoxy cyclohexane carboxylate), Epoxidation tetra benzyl alcohol, lactone denaturation epoxidation tetrahydro benzyl alcohol, Cyclohexene oxide, carboxylate, lactone denaturation epoxidation tetrahydro benzyl alcohol, Bisphenol A diglycidyl ether, Bisphenol F diglycidyl ether, diglycidyl ether, Bisphenol S diglycidyl ether, Hydrogenation bisphenol A diglycidyl ether, hydrogenation bisphenol F diglycidyl ether, Hydrogenation bisphenol A D diglycidyl ether, bromination bisphenol A diglycidyl ether, Bromination bisphenol F diglycidyl ether, bromination bisphenol S diglycidyl ether, Epoxy novolak resin, 1,4'-butanediol diglycidyl ether, 1,6'-hexanediol diglycidyl ether, glycerol triglycidyl ether, Trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, Polypropylene glycol diglycidyl ether, Ethylene glycol, Propylene glycol, By adding one sort or two sorts or more of alkylene oxide to aliphatic polyhydric alcohol, such as glycerin. The

monoglycidyl ether of diglycidyl ester species; aliphatic higher alcohol of poly glycidylethers; aliphatic series long chain dibasic acid of polyether polyol obtained: Phenol, cresol, Glycidyl ester species of monoglycidyl ether; higher fatty acid of polyether alcohol produced by adding alkylene oxide to butylphenol or these; Epoxidized soybean oil, Epoxy butyl stearate, epoxy stearic acid octyl, epoxidation linseed oil, etc. can be mentioned.

[0055] As other cationic polymerization nature organic compounds which can be used

additionally, For example, oxo orchid species, such as a tetrahydrofuran and a 2,3-dimethyltetrahydrofuran, A trioxane, Cyclic acetal, such as 1,3-dioxolane and 1,3,6-trioxane cyclooctane; Beta propiolactone, Annular lactone, such as epsilon-caprolactone; An ethylene sulfide, a 1,2-propylene sulfide, thirane [, such as thioepichlorohydrin,] - thietane [, such as 3,3-dimethyl thietane,] - ethylene glycol divinyl ether. Spiro orthoester species obtained by the reaction of a vinyl ether, epoxy compound and lactone, such as triethylene glycol divinyl

ether and trimethylopropane TORIBI nil ether, Vinylcyclohexane, Ethylene nature unsaturated compounds, such as isobutylene and polybutadiene; a derivative of each compound of these, etc. can be mentioned.

[0056] Polyol can be contained in order to make a resin composition of this invention reveal morphological stability (control performance of temporal modification) and property stability (control performance of a change with time of a mechanical property) of a cubic shape thing which are acquired by the photoresist of a resin composition, and the Mitsuzo form. Polyol used has 3-6 hydroxyl groups preferably in [one or more] one molecule. On the other hand, in using polyol containing a hydroxyl group exceeding six pieces into one molecule, there is a tendency for elongation and toughness of a cubic shape thing obtained to fail.

[0057] As this polyol, for example Trimethylopropane, glycerin, a compound containing a hydroxyl group more than trivalent [of a PENTAE listle oil, sorbitol, sucrose, a KUODO roll, etc.], Ethylene oxide (EO), propylene oxide (PO), butylene oxide, Polycaprolactone polyol obtained by denaturalizing by polyether polyol and a caprolactone which are obtained by denaturalizing with cyclic ether compounds, such as a tetrahydrofuran, Polyester polyol obtained by denaturalizing with polyester which consists of dibasic acid and diol can be mentioned. Specifically EO denaturation trimethylopropane, PO denaturation

trimethylopropane, Tetrahydrofuran denaturation trimethylopropane, caprolactone denaturation trimethylopropane, EO denaturation glycerin, PO denaturation glycerin, tetrahydrofuran denaturation glycerin, Caprolactone denaturation glycerin, EO denaturation pentaerythritol, PO denaturation pentaerythritol, Tetrahydrofuran denaturation pentaerythritol, caprolactone denaturation pentaerythritol, EO denaturation sorbitol, PO denaturation sorbitol, caprolactone denaturation sorbitol, EO denaturation sucrose, PO denaturation sucrose, although EO denaturation trimethylopropane, PO denaturation trimethylopropane, caprolactone denaturation trimethylopropane, PO denaturation glycerin, PO denaturation glycerin, and PO denaturation sorbitol are preferred, it is not limited to these illustration.

[0058] as the commercial item of polyol which can be used -- Sun Knicks TP-400, Sun Knicks GP-600, and Sun Knicks GP-1000, Sun Knicks SP-750, Sun Knicks GP-250, Sun Knicks GP-400, and Sun Knicks GP-600 (above) Mitsuniro -- Transformation, TMP-3 Glycol, and PNT-4, [Glycol and] EDA-P-4, EDA-P-8 (above, Japanese Emulsifier), G-300, G-400, G-700, T-400, EDP-450, SP-600, SC-800 (above) What can be obtained with trade names, such as Asahi Denka Kogyo K.K., TONE0301, TONE0305, TONE0310 (above, Union Carbide), the plaque cell 303, the plaque cell 305, and the plaque cell 308 (above, Daicel Chemical Industries, Ltd.), can be mentioned.

[0059] in a resin composition of this invention, an ethylene nature unsaturated monomer which

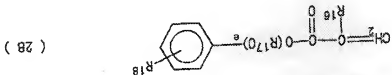
is a radical polymerization nature compound can be used together for improvement in mechanical strength of shaping material obtained, and shortening of modeling time. An ethylene nature unsaturated monomer is a compound which has an ethylene nature unsaturated bond (C=C) in a molecule, and can mention a monofunctional monomer which has one ethylene nature unsaturated bond in one molecule, and polyfunctional monomer which has two or more ethylene nature unsaturated bonds in one molecule.

[0060]As a monofunctional nature monomer which has one ethylene nature unsaturation bond groups in one molecule, For example, acryloyl morpholine (meta), 7-amino-3,7-dimethyloctyl (meta) acrylate, isobutoxymethyl(meta) acrylamide, isobornyl oxyethyl (meta) acrylate, isobornyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Ethyldiethylene-glycol (meta) acrylate, t-octyl(meta) acrylamide, dilacone (meta) acrylamide, dimethylaminooethyl (meta) acrylate, Diethylaminooethyl (meta) acrylate, lauryl (meta) acrylate, Dicyclopentadiene (meta) acrylate, JISHIKURC pentenyl (meta) acrylate, JISHIKURC pentenyl (meta) acrylate, N,N-dimethyl(meta) acrylamide tetra chlorophenyl (meta) acrylate, 2-tetrachlorophenoxyethyl (meta) acrylate, tetrahydrofurfuryl (meta) acrylate, tetrabromo phenyl (meta) acrylate, 2-tetrabromo phenoxyethyl (meta) acrylate, 2-trichlorophenoxy ethyl (meta) acrylate, tribromophenyl (meta) acrylate, 2-tribromophenoxyethyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, vinylcaprolactam, N-vinyl pyrrolidone, phenoxyethyl (meta) acrylate, butoxyethyl (meta) acrylate, Pentachlorophenyl (meta) acrylate,

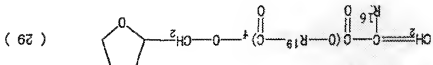
(meta) acrylate, pentabromophenyl (meta) acrylate, Polyethylene-glycol mono- (meta) acrylate, polypropylene-glycol mono- (meta) acrylate, being able to illustrate bormyl (meta-) acrylate, methyl TORIECHI range glycol (meta-) acrylate, and a compound expressed with following general formula (28) - (30), these are one-sort independent -- it is -- it can use combining two or more sorts.

[0061]

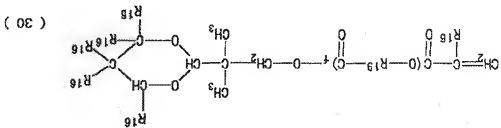
[Formula 27]



[Formula 28]



[Formula 29]



(General formula (28) In - (30), R^{16} a hydrogen atom or a methyl group) [show and] R^{17} -- 2-6 carbon atoms -- the alkylene group of 2-4 is shown preferably -- R^{18} -- a hydrogen atom or 1-12 carbon atoms -- the alkyl group of 1-9 is shown preferably -- R^{19} -- 2-8 carbon atoms -- the alkylene group of 2-5 is shown preferably, e -- 0-12 -- it is an integer of 1-8 preferably -- f -- 1-8 -- it is an integer of 1-4 preferably.

these monofunctional nature monomers -- among them, although isobornyl (meta-) acrylate, lauryl (meta-) acrylate, and phenoxyethyl (meta-) acrylate are preferred, it is not limited to these illustration.

[0062]As a commercial item of these monofunctional nature monomers, for example, ARONIKKUSU M-101, M-102, M-111, M-113, M-117, M-152, TO-1210 (above) Toagosei, Inc., Kaya Rudd TC-110S, R-564, R-128H (above) Nippon Kayaku Co., Ltd., screw coat 192, screw coat 220, and screw coat 231H.P., An available thing can be mentioned with trade names, such as the screw coat 2000, the screw coat 2100, the screw coat 2150, the screw coat 8F, and the screw coat 17F (above, OSAKA ORGANIC CHEMICAL INDUSTRY, LTD.).

[0063]As a polyfunctional monomer which has two or more ethylene nature unsaturation bond groups in one molecule, for example, ethylene glycol di(metha)acrylate, tetraethylene glycol di(metha)acrylate, triethylene glycol di(metha)acrylate, tri(metha)acrylate, Tris(2-hydroxyethyl)isocyanurate tri(metha)acrylate, Caprolactone denaturation tris(2-hydroxyethyl)isocyanurate tri(metha)acrylate, TORIMECHI roll pro pantry (meta) acrylate, EO denaturation TORIMECHI roll pro pantry (meta) acrylate, PO denaturation TORIMECHI roll pro pantry (meta) acrylate, Tori propylene glycol di(metha)acrylate, Neopentyl glycol di(metha)acrylate, both-ends (meta) acrylic acid adducts of bisphenol A diglycidyl ether, 1,4-butanediol di(metha)acrylate, 1,6-hexanediol di(metha)acrylate, Penta ERIS RITORTORI (meta) acrylate, pentaerythritol tetra (meta) acrylate, Polyester TERULI (meta) acrylate, poly ethylene glycol di(metha)acrylate, Dipentaerythritol tetra (meta) acrylate, caprolactone denaturation dipentaerythritol hexa (meta) acrylate, Caprolactone denaturation dipentaerythritol penta (meta) acrylate, Dilitmethyol propane tetra (meta) acrylate, EO denaturation bisphenol A di(metha)acrylate, PO denaturation bisphenol A di(metha)acrylate,

acrylate, EO denaturation hydroxylation bisphenol A di(meth)acrylate, PO denaturation hydroxylation bisphenol A di(meth)acrylate, EO denaturation bisphenol F di(meth)acrylate, being able to illustrate acrylate (meta-) or phenol novolac poly glycidyl ether, etc., these are one-sort independent -- it is -- it can use combining two or more sorts.

[0064]these polyfunctional monomers -- inside and TORIMECHI roll pro pantry (meta-) acrylate, EO denaturation TORIMECHI roll pro pantry (meta) acrylate, PO denaturation TORIMECHI roll pro pantry (meta) acrylate, Penta ERIS RITORUTORI (meta) acrylate, pentaerythritol tetra (meta) acrylate, Dipentaerythritol tetra (meta) acrylate, caprolactone denaturation penta (meta) acrylate, Although caprolactone denaturation dipentaerythritol hexa (meta) acrylate and ditrimethylol propane tetra (meta) acrylate are preferred, it is not limited to these illustration.

[0065]As a commercial item of these polyfunctional monomers, For example, SA1002 (above, Mitsubishi Chemical, Inc.), screw coat 195, screw coat 230, screw coat 260, screw coat 215, screw coat 310, and screw coat 214H.P., The screw coat 295, the screw coat 300, the screw coat 360, screw coat GPT, The screw coat 400, the screw coat 700, the screw coat 540, the screw coat 3000, the screw coat 3700 (above) OSAKA ORGANIC CHEMICAL INDUSTRY, LTD., Kaya Rudd R-526, HDDA, NPGDA, TPGDA, MANDDA, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPPTA, THE-330, DPHA, and DPHA-2H, DPHA-2C, DPHA-2I, D-310, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, IPA-320, IPA-330, RP-1040, RP-2040, R-011, R-300, R-205 (above, Nippon Kayaku Co., Ltd.), ARONIKIKUSU M-210, M-220, M-233, M-240, M-215, M-305, M-309, M-310, M-315, M-325, M-400, M-6200, M-6400 (above) Toagosei, Inc., light acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA, DCP-A (above, Kyoetsu Fatty chemistry Industry), New frontier BPE-4, TEICA, BR-42M, GX-8345 (above) Dai-ichi Kogyo Seiyaku Co., Ltd., ASF-400 (above, Nippon Steel Chemical Co., Ltd.), A thing of acquisition can be mentioned with trade names, such as R1POKISHI SP-1506, SP-1507, SP-1509, VR-77, SP-4060 (above, Showa High Polymer Co., Ltd.), and NK ester A-BPE-4 (above, Shin-Nakamura Chemical Co., Ltd.).

[0066]The Tori (meta) acrylate compound illustrated above as this polyfunctional monomer, A tetra (meta) acrylate compound, a penta (meta) acrylate compound, A hexa (meta) acrylate compound is preferred and among these TORIMECHI roll pro pantry (meta) acrylate, EO denaturation TORIMECHI roll pro pantry (meta) acrylate, dipentaerythritol hexa (meta) acrylate, Although dipentaerythritol penta (meta) acrylate and especially ditrimethylol propane tetra (meta) acrylate are preferred, it is not limited to these illustration.

[0067]When blending an ethylene nature unsaturated monomer with a resin composition, in order to make the radical polymerization reaction start, a radical character photopolymerization initiator is also usually added. By receiving energy lines, such as light, it decomposes, and with

a free radical by which it is generated, a radical character photopolymerization initiator is a compound which makes a radical polymerization reaction of an ethylene nature unsaturated monomer start, and can use the usual radical character photopolymerization initiator. [0068] The usual radical character photopolymerization initiator can be used as a radical character photopolymerization initiator. For example, an acetophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-isobutane 1-one, Carbazole, xanthone, 4-chlorobenzo phenon, 4,4'-diaminobenzophenone, 1,1'-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-methoxybenzophenone, A thioxan ton system compound, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino propan-2-one, 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl)- Butan-1-one, A triphenylamine, 2,4,6-trimethyl benzoyl diphenylphosphine oxide, Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl BENCHIRU phosphine oxide, Benzyl fluorone, a fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, a Michler's ketone, 3-methylacetophenone, Combination with another 3,3',4,4'-tetra(4-butyl par oxy-carbonyl) benzophenone (BTB) and BTB and xanthene, thioxanthene, coumarin, keto coumarin, and dye sensitizing agent, etc. can be mentioned. Among these Benzyl dimethyl ketal, 1-hydroxycyclohexylphenyl ketone, 2,4,6-trimethyl benzoyl diphenylphosphine oxide, 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl)- Although especially butan-1-one etc. are preferred, it is not limited to these illustration.

[0069] As an ingredient blended with a resin composition if needed other than cationic polymerization nature or a radical polymerization nature organic compound, Triethanolamine, methyldiethanolamine, triethylamine, A photosensitizer which consists of amine system compounds, such as diethylamine (polymerization accelerator), A thioxan ton, A derivative of a thioxan ton, a derivative of anthraquinone and anthraquinone, A derivative of anthracene and anthracene, a derivative of perylene and perylene, A photosensitizer which consists of benzophenone, benzoin iso-propyl ether, etc.; reactive diluent, such as vinyl ether, vinylsulfides, vinyl urethane, urethane acrylate, and vinyl urea, can be mentioned.

[0070] Various kinds of additive agents may contain in a resin composition of this invention. Epoxy resins other than an epoxy group containing compound (B) explained as a cationic polymerization nature organic compound as this additive agent in a top, and other epoxy compounds, Polyamide, polyamidimide, polyurethane, polybutadiene, polychloroprene, Polyester, styrene butadiene styrene block copolymer, Petroleum resin, xylene resin, ketone resin, cellulosic resin, fluorene system oligomer, Polymer, such as silicone series oligomer and polysulfide system oligomer, thru/or oligomer, Polymerization inhibitor, such as phenothiazin and 2,6-di-tert-butyl-4-methylphenol, other polymerization start auxiliary agents and antiaging agents, a leveling agent, a wettable improving agent, a surface-active agent, a plasticizer, UV stabilizer, an ultraviolet ray absorbent, a silane coupling agent, paints, a color,

etc. can be mentioned. In a resin composition of this invention, an inorganic bulking agent, an organic bulking agent, etc. may contain, as an inorganic bulking agent, inorganic solid particles and boric acid aluminum system compounds, such as a glass bead, talc particles, and oxidized silicon. A whisker etc. which consist of a basic-magnesium-sulfate system compound, an aluminum oxide, and an oxidized silicon system compound are mentioned. Organic solid particulates etc. which consist of bridge construction polystyrene system polymers, constructed type polymethacrylate system polymers of a bridge, polyethylene system polymers, polypropylene system polymers, etc. as an organic bulking agent are mentioned. What processed these inorganic bulking agents and an organic bulking agent by silane coupling agents, such as an aminosilane system, an epoxysilane system, and an acrylic silane system, can be used.

A resin composition of preparation this invention of a resin composition can be prepared by mixing an ingredient and various additive agents uniformly in addition it is blended an above-mentioned (A) ingredient - (C) ingredient and if needed.

[0071] An obtained resin composition is useful as a photo-setting resin constituent for optical solid modeling. In that case, it is preferred to have the viscosity of 50 - 10000cP for this resin composition in 25 **, and it is 100 - 5000cP more preferably.

A resin composition of this invention which is more than optical solid modeling and is produced by making is suitably used as liquefied resin material of a photoresist in the optical solid modeling method. That is, a cubic shape thing of desired shape can be manufactured to a resin composition of this invention by the optical solid modeling method which irradiates with lights, such as visible light, ultraviolet radiation, and infrared light, selectively, and supplies energy required for hardening.

[0072] Especially as a means to irradiate a resin composition selectively regarding the place, it is not restricted and various means can be adopted. For example, convergence light etc. which were obtained using a laser beam, a lens, a mirror, etc. as a light source can be used. A means to make the convergence light scan on a resin composition, and a mask which has a light transmission section of a predetermined pattern are used. A means to irradiate a resin composition via an optical fiber corresponding to a predetermined pattern in this light guide member etc. are employable using a means to irradiate a resin composition with non-convergence light via this mask, and a light guide member, by which it comes to bundle many optical fibers. In a means using a mask, what forms electrooptically a mask image which consists of a light transmission area and a light impermeability field by the same principle as a liquid crystal display according to a predetermined pattern can also be used as a mask. When it is what a cubic shape thing carried out above with the purpose has a detailed portion, or close dimensional accuracy is required as, it is preferred to adopt a means to scan a laser beam with a small spot diameter as a means to irradiate a resin composition

selectively.

[0073] Irradiated planes (for example, scanning plane of convergence light) of light in a resin composition accommodated in a container may be any of an oil level of the resin composition concerned, and a contact surface with a container wall of a translucency container. When making an oil level of a resin composition, or a contact surface with a container wall into an irradiated plane of light, it can irradiate with light via direct or a container wall from the exterior of a container.

[0074] In the aforementioned optical solid modeling method, after stiffening a particular part of a resin composition, by moving an irradiation position (irradiation surface) of light to an uncured part continuously or gradually from a hardened portion, a hardening portion is made to laminate and it is usually considered as desired cubic shape. Here, movement of an irradiation position can be performed by various methods, for example, methods, such as moving any of hardened portions of a light source, a receiving container of a resin composition, and a resin composition they are, or carrying out additional supply of the resin composition to the container concerned, can be mentioned.

[0075] If a typical example of the aforementioned optical solid modeling method is explained, by carrying out fine amount descent (sedimentation) of the supporting stage which rise and fall can control freely in a receiving container from an oil level of a resin composition, on the supporting stage concerned, a resin composition will be supplied and the thin layer (1) will be formed. Subsequently, a cured resin layer (1) of a solid state is formed by irradiating with light selectively regarding the place with a prescribed pattern to this thin layer (1). Subsequently, by supplying a resin composition on this cured resin layer (1), forming that thin layer (2), and carrying out an optical exposure selectively regarding the place with a prescribed pattern to this thin layer (2), a new cured resin layer (2) is formed so that this may be followed on said cured resin layer (1) and it may laminate in one. And a cubic shape thing in which it comes to laminate two or more cured resin layer (1) - (n) in one is modeled by prescribed frequency (n times) repeating this process, without making it change, changing a pattern by which an optical exposure is carried out according to the target cubic shape.

[0076] Thus, a cubic shape thing obtained is picked out from a receiving container, and after removing an unreacted resin composition which remains on the surface, it washed if needed. As a detergent here Alcohol system organic solvents, such as isopropyl alcohol and ethyl alcohol, Thermosetting resin and a photo-setting resin of an organic solvent and hypoviscosity which are represented by ester system organic solvents, such as ketone system organic solvents, such as acetone and methyl ethyl ketone, and ethyl acetate, terpenes, and glycol ether system ester species can be mentioned.

[0077] To manufacture a good cubic shape thing of surface smoothness when washing, it can wash using said thermosetting resin or a photo-setting resin, and it is necessary to perform a

post cure by a heat exposure or optical exposure in this case according to a kind of hardening resin used for washing. Since the post cure can also stiffen an unreacted resin composition which it not only stiffens surface resin, but has remained inside a cubic shape thing, also when an organic solvent washes, it can perform a post cure.

[0078] Thus, a cubic shape thing obtained has a mechanical strength, high dimensional accuracy, etc., and is excellent also in heat resistance. The cubic shape thing concerned is excellent in morphological stability and property stability, and can be conveniently used also as a prototype for function confirmation, etc.

[0079] In order to raise surface intensity of a cubic shape thing, and heat resistance, after performing washing processing, it is preferred to use hard coat material of thermosetting or a photoresist. As this hard coat material, organic coat material which consists of an acrylic resin, an epoxy resin, silicone resin, etc., or an inorganic hard coat can be used, and these hard coat material is independent one sort, or can be used combining two or more sorts of things. [0080]

[Example] Hereafter, although the example of this invention is described, this invention is not limited to these examples.

The combination formula shown in <Example 1> table 1 is followed, and it is as a (A) ingredient [(1,4-screw), [(3-ethyl-3-OKISETA nil methoxy) Methyl] EPOLEAD PB3600 which is the epoxy denaturation polybutadiene which are 90 weight sections and the (B) ingredient about benzene Nine weight sections, (C) The transparent liquid composition was obtained by teaching as an ingredient UVI-6974 (passage above-mentioned [made in Union Carbide and the contents] 1 weight section, in an agitation vessel, and agitating at 60 ° for 1 hour.

According to the combination formula shown in <Examples 2-5> table 1, the transparent liquid resin composition was obtained like Example 1 except in addition to this having chosen the ingredient from (A) - (C) ingredient and that of a case as a combination ingredient. [0081] According to the combination formula shown in the <comparative example 1-4> table 1, the transparent liquid resin composition (resin composition for comparison) was obtained like Example 1 except having chosen the ingredient of the display as a combination ingredient.

Each resin composition has the following features.

A Comparative example 1: (B) ingredient is not included.

3,4-epoxycyclohexymethyl 3,4'-epoxy cyclohexane carboxylate is included instead of a

Comparative example 2: (A) ingredient.

A Comparative example 3: (B) ingredient is not included.

Comparative example 4: They are epoxy / acrylic monomer hybrid type photo-setting resin

constant.

3 g of 2,6-di-tert-butyl-4-methylphenol was taught to the reaction vessel provided with the

<comparative example 5> urethane acrylate type photo-setting resin constituent urethane

acrylate composition agitator as 3311 g of isophorone diisocyanate, 10g of dibutyltin dilaurate, and polymerization inhibitor. Next, 1730 g of hydroxyethyl acrylate was added, controlling temperature at 20 ° or less. After addition and after continuing churning at further ten to 20 ° for 1 hour, polyesterdiol "P-1010" (Made by Kuraray) 745g of the number average molecular weight 1000 which consists of 3-methyl-1,5-pentanediol and adipic acid was added maintaining at 40 to 50 ° temperature. Subsequently, after continuing churning at 50-60 ° for 5 hours, the reaction was terminated and the number average molecular weight obtained about 1680 urethane acrylate [U-1].

[0082] To the reaction vessel provided with the preparation agitators of a liquid resin composition, urethane acrylate [U-1] 36 weight sections, Tricyclodecane diyl dimethylene diacrylate was carried out as a reaction diluent by 18 weight sections, isobornyl acrylate 23 weight section, and AKURORIRU morpholine 16 weight section, agitation mixing of the 1-hydroxyphenyl ketone 7 weight section was carried out at 50-60 ° as a photoinitiator, and the transparent-liquid-resin constituent was obtained.

[0083]
[Table 1]

| (A)成分 | 比較例 | | | | |
|---------------------------|-----|----|----|----|----|
| | 1 | 2 | 3 | 4 | 5 |
| 1,4-ビス(3-エチル-3-オキセニル)エーテル | 90 | 75 | 70 | 63 | 58 |
| 924 | 99 | | | | 75 |
| (B)成分 | 9 | 24 | 9 | 21 | 18 |
| 24 | | | | | |
| (C)成分 | 1 | 1 | 1 | 1 | 1 |
| UVI-6974 | 1 | | | | |
| 3,4-エポキシジフェニルエーテル | 20 | | | | |
| 75 | 24 | 49 | | | |
| 1,4-ビス(3-エチル-3-オキセニル)エーテル | 21 | | | | |
| 14 | | | | | |
| 8 | | | | | |
| 14 | | | | | |
| 14 | | | | | |
| 17 | | | | | |
| 18 | | | | | |
| 36 | | | | | |
| 7 | | | | | |
| 1 | | | | | |
| 16 | | | | | |
| 23 | | | | | |
| 16 | | | | | |

[0084] About each of the photo-setting resin constituent obtained by the <evaluation of resin

2.

composition> examples 1-5, and the comparative examples 1-5, the hardenability of resin liquid, the toughness of a hardening film, and the modeling nature of the cubic shape thing were evaluated in accordance with the following valuation method. A result is shown in Table [Hardenability of resin liquid] The hardenability of resin liquid is a grade (the degree of hardening) of the polymerization reaction of a resin composition, and crosslinking reaction over the dose of light.

The degree of hardening affects the dynamics physical properties of a hardened material, for example, Young's modulus, the rate of bending flexibility, etc. That is, that a photoresist is good means that the dynamics physical properties of the hardened material obtained do not change even if irradiation light quantity changes. In this invention, it carried out by measuring the Young's modulus of the cured resin film produced under a different dose in evaluation of the hardenability of resin liquid.

Production of a specimen : (1) By applying a resin composition on a glass plate using an applicator, The 200-micrometer-thick coating film was formed, the surface of the coating film concerned was irradiated with ultraviolet rays using the conveyor hardening device (the product made from Eye Graphics; UB0311-00 type) equipped with a metal halide lamp, and the cured resin film was produced. The dose of ultraviolet rays was made into 100 mJ/cm^2 or 500 mJ/cm^2 . From setting the produced cured resin film for 1 hour into the air-conditioned room of the temperature of 23 **, and 50% of relative humidity, the specimen was prepared and measurement was presented.

(2) Young's modulus measurement : Young's modulus was measured on with speed-of-testing 1 mm/min and a distance between the marked lines of 25 mm conditions about the specimen produced with each dose in the air-conditioned room of the temperature of 23 **, and 50% of relative humidity. The tension tester (the Shimadzu Corp. make, AUTOGGRAPH AGS-IKND) performed measurement.

[0085]Toughness of a hardening film] The toughness of a hardened material expresses the difficulty of breaking by the stress given from the outside. There is elongation after fracture as the index. In this invention, evaluation of the toughness of a hardening film was performed by measuring the elongation after fracture of a cured resin film.

(1) By applying a resin composition on a glass plate using the creation applicator of a specimen, The 200-micrometer-thick coating film was formed, the surface of the coating film concerned was irradiated with ultraviolet rays using the conveyor hardening device equipped with a metal halide lamp (dose 500 mJ/cm^2), and the exposure was stopped before hardening thoroughly. In this way, the semi-hardening resin film was produced. Subsequently, the semi-

hardening resin film was exfoliated from the glass plate, and it put on the release paper, and with the field which irradiated with ultraviolet rays first, it irradiated with the ultraviolet rays from the field of an opposite hand (dose 500 mJ/cm²), and the cured resin film was produced. [0086] By settling the created cured resin film for 24 hours into the air-conditioned room of the temperature of 23 **, and 50% of relative humidity, the specimen was created and measurement was presented.

(2) Elongation after fracture was measured with the aforementioned tension tester on with speed-of-testing 50 mm/min and a distance between the marked lines of 25 mm conditions in the air-conditioned room of the elongation-after-fracture measurement temperature of 23 **, and 50% of relative humidity.

[Modeling nature of a cubic shape thing] Evaluation of the modeling nature of a cubic shape thing was performed by measuring the time which the dimensional accuracy of the cubic shape thing modeled from each resin liquid and modeling took.

Modeling of a cubic shape thing : (1) Using each of the resin composition prepared by Examples 1-5 and the comparative examples 1-5 with an optical shaping apparatus (trade name solid creator SCS-1000HD, Sony Corp. make). According to the following modeling conditions, the H type cubic shape thing shown in drawing 1 with the front view was modeled. In both beams with a target dimension of this shaped object level on two pillars which constitute H, a section consists of one-side a square pillar it is [square pillar] a square it is [square] 6.4 mm, and the length of a pillar is [the length of a beam] 88.8 mm in 44.5 mm. Other target dimensions are as a graphic display.

[0087] The modeled cubic shape thing carried out state adjustment by settling for 24 hours into the air-conditioned room of the temperature of 23 **, and 50% of relative humidity. laser beam intensity: in a <modeling condition> (i) oil level -- 10-mW/(ii) scan speed: -- in each resin composition, proper scan speed (iii) from which hardening depths are set to 0.15 mm -- thickness [of the cured resin layer to form] : -- number-of-times of 0.1mm/(iv) lamination: -- measurement [of the dimensional accuracy of 445 times cubic-shape / (2) / thing] : -- in obtained H type cubic shape thing, The actual width A, B, and C of the cubic shape thing in each position of a of drawing 1, b, and c was measured to 0.01 mm using measurable slide calipers, and the dimensional accuracy of the cubic shape thing was evaluated from the difference of the dimension a for which it asked by following formula (i) and (ii), and B, and the difference of the sizes C and B.

[0088]

Difference in dimension of AB = (A-B) (i)

Difference in dimension of CB = (C-B) (ii)

(3) In the modeling time-measurement above-mentioned optical shaping apparatus, the time

taken to model H type cubic shape thing of drawing 1 was measured.

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example 5 which is urethane acrylate type photo-setting resin constituents take modeling the cubic shape thing of drawing 1 was 10 or less hours. On the other hand, in the comparative example 1, intensity of the resin hardened by the laser radiation generally called green strength was not able to model the target cubic shape thing low. It required for modeling according to the comparative examples 2 and 4 for 20 hours or more.

- Although the shaping material difference in dimension excelled [shaping material] in Examples 1-5 and the comparative examples 2 and 4 small was obtained in respect of dimensional accuracy, in the shaping material of the comparative examples 3 and 5, difference in dimension was large and sufficient dimensional accuracy for a Mitsuzo form use was not acquired.

[0090]

[Effect of the invention]According to the photo-setting resin constituent for optical solid modeling of this invention, modeling is completed for a short time, since cure shrinkage is small, dimensional accuracy is high, the outstanding photoresist promptly hardened by optical exposure can be obtained, and the cubic shape thing excellent in a mechanical strength, especially toughness can be obtained easily.

[Translation done.]